Workshop on X-rays and Nano-Science
Wednesday, November 1, 2000

9:00 Wai Kwok (Opening remarks)

-----------------Chair: George Crabtree------------------

9:05 Lin Chen (CHM)
Probing Transient Molecular Structures with Laser Pump/X-ray Probe Time-Domain XAFS

9:20 *Lynda Soderholm (CHM)
Atomic Scale Characterization of Nanosized Aggregates and Clusters

9:40 Hoydoo You (MSD)
Synchrotron X-ray Study of Nano-Scale Materials during Self-Assemblies at/near Liquid/Solid Interfaces

9:55 *Tijana Rajh (CHM)
Extended Charge Separation in TiO_2 Nanoparticles Linked to DNA-Oligonucleotides

10:15 Barry Lai (APS)
X-ray Microprobe and its Applications

10: 30 Yong Chu (APS)
New Approach to Microdiffraction

-----------------Chair: Sam Bader------------------------

10:45 Brian Stephenson (MSD)
In-situ Studies of Nanostructure Fabrication Processes

11:00 Dimitri Argyriou (MSD)

11:15 George Srajer (APS)
Magnetic Imaging with a Circularly Polarized Microprobe

11:30 John Freeland (APS)
Characterizing Nanostructures with Polarized Soft X-rays

11:45 Stephen Streiffer (MSD)
Ferroelectric Nanostructures

12:00 Juan Carlos Campuzano (UIC/MSD)
Photoemission for NanoScience

12:15 Adjourn

talks will be 10mins with 5 mins for questions. except for (*) which are 15mins with 5 mins for questions

Probing Transient Molecular Structures with Laser Pump/X-ray Probe Time-Domain XAFS

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The molecular structures of short-lived reaction intermediates in photoinduced processes are captured by laser pump/X-ray probe time-domain XAFS experiments using X-rays from the APS. These structural information allows us to have new insights of photoinduced electron and energy transfer processes in nanostructures for establishing structure/function relationships. The current capability and potential future research directions in nanosciences will be discussed.

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Atomic Scale Characterization of Nanosized Aggregates and Clusters

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The f-Electron Interactions group relies heavily on synchrotron-based research, particularly on X-ray absorption spectroscopy (XAS) and, more recently, on high-energy scattering. Our XAS experiments center on the speciation of metal ions in clusters and in solution. Specifically, we have developed expertise in quantifying metal-ion oxidation states and redox properties using in situ x-ray electrochemical techniques. The data obtained from these experiments allow a detailed characterization of the redox behaviour of components of complex clusters. The data from high-energy scattering experiments serves to complement the XAS studies. By determining pair-distribution functions (PDF's) from the scattering data, it is possible to probe the atomic arrangement and structures within small "amorphous" nanoclusters. Examples of these techniques as they pertain to nanoparticles will be discussed.

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SYNCHROTRON X-RAY STUDY OF NANO-SCALE MATERIALS DURING SELF-ASSEMBLIES AT/NEAR LIQUID/SOLID INTERFACES

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Most solid surfaces are covered by (aqueous) liquid in our surroundings as the thermodynamics dictates a thin liquid layer to intervene the solid/gas interfaces in moist air. Also, the liquid/solid interfaces are possibly excellent environments for incubating nano-scale self-assemblies. Despite the potential importance, studies of the liquid/solid interfaces have been hampered by the difficulties associated with the presence of the liquid layer adversely affecting many of our experimental probs. Use of (synchrotron) x-rays techniques alleviate this difficulty due to x-rays' ability to penetrate yet sufficiently sensitive to nano-size objects at the interfaces.

The nano-scale objects trapped at or near the interfaces of liquid/solid may undergo self-assembling processes via mutual repulsive interactions governed by thermodynamic, kinetic, biological, and/or unknown processes. The detailed natures of self-assembly are subjected to experimental variables, such as temperature, pH, viscous sheer stress, and electric field, and to physical/chemical properties of solid surface, nano-particles (or molecular building blocks), and solution.

The self-assembling processes may include, but not limited to, adsorption and self-organization of nano-size objects, deposition processes inducing the nano-size objects and their self-organization, etching/corrosion processes inducing the substrate to pattern itself, deposition of additional materials to and through the nano-scale crevices and holes.

We will discuss a few examples of others and ours, found in previous studies of solid/water interfaces. They will include 1) self-assembly of extremely anisotropic porous silicon during galvanostatic etching [hy1,hy2], 2) self-assembly of nano-size Rh clusters

[hy3], and 3) fascinating example of self-assembly of biologically modified nano-particles [hy4]. We will also discuss possibilities of nano-scale sedimentation, nano-scale interface evolution, and nano-sphere lithography [hy5] issues associated with nano-size length scales.

In all of these examples, synchrotron x-ray techniques applied in-situ during self-assembling processes will enable us to study the details of self-assembly processes and possibly also to discover new self-assembled systems and new self-assembling mechanisms. In particular, substrates pre-designed (using fab facility or other means) offer exciting opportunities of studying self-assemblies previously undiscovered or unimaginable.

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*Collaborators include Z. Nagy (MSD) and Y. Chu (XFD).

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Extended Charge Separation in TiO_2 Nanoparticles Linked to DNA-Oligonucleotides

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Sequence specific sensing of DNA is a topic of significant interest of because unique applications in the fields of diagnostics, genome sequencing, forensics, assays, and drug affinity studies. In this work we are binding DNA oligonucleotides to the surface of modified TiO_2 nanoparticles (50 Å) designed to retain the functional properties of the linked biomolecules. Nanocrystalline metal oxide semiconductor particles act as miniaturized electrochemical cells and when linked to biologically active molecules function as site selective electronic transducers. The biological molecules linked to the nanoparticle can provide binding specificity through the design of the biomolecule linked to the nanoparticle. We also report selective functions of the nano-paprticle that is enabled through light induced charge separation in semiconductor particles, followed by hole scavenging by the biological molecule linked to the nanoparticle. Therefore, extended charge separation in these systems is a fingerprint of DNA hybridization. This forms a basis for a completely new family of DNA-based sensors that operate on the principles of DNA-mediated photoinduced charge separation in nanocrystalline semiconductors. Moreover, this approach will permit novel intracellular manipulation of DNA, RNA, and proteins for gene surgery/gene therapy, structure determination, drug delivery, footprinting (determination of position of protein binding on DNA), DNA repair, and other similar functions. Selective photocleavage of DNA that results in fragmentation of DNA at desired sites is of special interest because it can result in the development of novel approaches for manipulation of DNA at the molecular level, not only *in vitro* but also *in situ* and *in vivo*. Gene therapy is the correction of a genetic disorder either by introducing new genetic information into a cell or altering the genetic content of a cell. We also report the introduction of oligonucleotide-bound nanoparticles into cellular nuclei and retention of these particles based on genomic copy-number of the oligonucleotide sequence.

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L. X. Chen, T. Rajh, Z. Wang and M. C. Thurnauer
J. Phys. Chem. B, 101, 10688-10697 (1997)

CHARGE-TRANSFER REACTIONS ON THE SURFACE OF NANOMETER-SIZED SEMICONDUCTOR PARTICLES
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Trends in Heat, Mass & Momentum Transfer, 3 1-17 (1997)

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Tijana.Rajh, Jovan Nedeljkovic, Lin X. Chen, David M. Tiede and Marion C. Thurnauer
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STRUCTURAL CHARACTERIZATION OF SELF ORGANIZED TiO_2 NANOCLUSTERS STUDIED BY SMALL ANGLE NEUTRON SCATTERING
T. Rajh, M. C. Thurnauer, D. M. Tiede and P. Thiyagarajan
J. Phys. Chem. B, 103, 2172-2177 (1999)

X-RAY ABSORPTION REVEALS SURFACE STRUCTURE OF TITANIUM DIOXIDE NANOPARTICLES
L. X. Chen, T. Rajh, W. Jager, J. Nedeljkovic and M. C. Thurnauer
J. of Synchrotron Radiation, 6, 445-447 (1999)

IMPROVING OPTICAL AND CHARGE SEPARATION PROPERTIES OF NANOCRYSTALLINE TiO_2 BY SURFACE MODIFICATION WITH VITAMIN C
T. Rajh, J. Nedeljkovic, L. X. Chen, O. Poluektov and M.C. Thurnauer
J. Phys. Chem. B, 103, 3515-3519 (1999)

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X-ray Microprobe and its Applications

Barry Lai
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The x-ray microprobe at 2-ID of the SRI-CAT produces a submicron x-ray spot in the hard x-ray regime of 6-30 keV. Techniques that had been developed included microdiffraction, fluorescence microanalysis, microtomography, and transmission full-field imaging. These techniques had attracted various materials applications from users, such as mapping of local strain, crystallographic phase, dislocation, and composition. Examples of these applications will be presented.

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New Approach to Microdiffraction

Yong Chu

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Diffractometers currently in use are designed for conventional x-ray sources, which produce mm-size beams. While x-ray beams have been dramatically reduced in size due to advances in focusing optics, the accuracy of diffractometer motions still remains around 30~50 microns. A new approach to solve the circle of confusion problem will be discussed in the presentation.

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In-situ Studies of Nanostructure Fabrication Processes.

Brian Stephenson
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In order to fabricate nanostructures in the wide range of materials to be studied at CNM (e.g. metals and alloys, multicomponent oxides, diamond), a variety of patterning processes must be developed and optimized. These include 'additive' techniques such as selective or templated deposition from vacuum, vapor, or solution, as well as 'subtractive' techniques such as focused ion beam sputtering or reactive ion etching. The extraordinary capabilities of x-ray techniques at APS provide opportunities to perform in-situ studies of these processes, both as a means to efficiently optimize nanostructure fabrication, and to develop understanding of the science of patterning at the nanoscale. In particular, I will discuss in-situ surface scattering and microdiffraction during processing to understand morphology development and defect formation. Unique characteristics of the APS, such as the availability of higher energies to penetrate environments and allow access to a wide range of reciprocal space, and high brilliance to give high Q resolution in microbeams with sufficient intensity for time-resolved studies, will allow outstanding in-situ x-ray studies of nanostructure fabrication processes at CNM.

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Magnetic Imaging with a Circularly Polarized Microprobe

George Srajer

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We report on the development of a circularly polarized x-ray microprobe in the intermediate energy range from 5 to 10 keV. By combining microfocusing capabilities with magnetic x-ray scattering techniques, this probe extends x-ray imaging techniques to the measurement of the micron-scale magnetic distribution within the sample. Previous work in this field has been performed in the soft x-ray regime. This probe, on the other hand, is designed for hard x-rays, which allows for the ability to probe buried magnetic structures. The properties of the microprobe were characterized, and the technique was applied to the two-dimensional mapping of magnetic domains in $HoFe_2$ and SmCo/Fe

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Characterizing Nanostructures with Polarized Soft X-rays

John Freeland

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Ferroelectric Nanostructures

Stephen Streiffer
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Ferroelectrics are currently making the transition into several classes of microelectronic devices, and significant opportunities exist to develop innovative nanoscale devices/technologies, if techniques for fabricating and integrating ferroelectric nanostructures can be perfected. Ferroelectric materials exhibit long-range cooperative phenomena in many ways analogous to those found in ferromagnetic and superconducting systems, and which lead to a large variety of useful materials properties (electromechanical, electrooptic, nonlinear dielectric, etc.). In this presentation, an introduction will be given to state-of-the art exploration of ferroelectrics at the micro- and nanoscale based on work at ANL and elsewhere. Fundametal scientific issues which improved facilities would enable us to address, will be discussed.

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Photoemission for Nanoscience

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Photoemission is the ideal tool for providing information on the electronic structure of materials. It can also be used as a holographic tool, providing information on the geometrical structure. The main limitation so far has been its surface sensitivity, arising from the need to use low photon energies in order to obtain sufficient momentum and energy resolution. Recently, the advent of several technologies have dramatically increased the usefulness of this technique. Examples are: high resolution spectrometers, together with high resolution and high photon energy beamlines eliminate the surface sensitivity problem; photoemission microscopes allow the collection of both structural and spectroscopic data at nanoscales; and finally, the development of holographic techniques allow the direct observation of atomic structure that does not have long range order. We propose to build a facility at the APS that will provide state of the art research and nano-characterization.